where t_s is the setting point in °C., P the number of repeating units in the chain, and a and b constants. The experimental data covered molecules with from 54 to 558 atoms in the straight chain, a much wider range than has previously been available for pure compounds. At that time it was duly noted that this homologous series did *not* follow the logarithmic freezing point equation deduced from what might be termed "kinetic" considerations by Austin[2] but the authors could offer no explanation for the form of the equation actually obtained.

Very recently, however, a publication has appeared by Huggins[3] concerning the properties of long-chain compounds; it includes the derivation on purely thermodynamic grounds of a general law relating the freezing points in a polymer-homologous series to the number of atoms in the chain. This equation is

$$T_f = (A + Bn)/(C + Dn) \qquad (2)$$

where T_f is the absolute freezing point, n the number of atoms in the straight chain and the other symbols are constants. Inspection of the empirical relationship (1), and substituting for t_s its equivalent $T_f - 273$, reveals that this equation is identical in form with that of Huggins. This provides excellent support for the latter over a very wide range of chain lengths, many times greater than is possible in the n-alkane series, agreement for which (up to C_{70}) is shown by the previous work of Garner[4] and co-workers, who also have attempted to justify their results theoretically.[5] In both series the relation fails for chains of less than 20 atoms.

The agreement thus found between Huggins' thermodynamically derived freezing point equation and the freezing point data for the higher polyoxyethylene glycols is important additional evidence for the purity (uniformity of chain length) of this series of synthetic polymers.

[2] Austin, This Journal, **52**, 1049 (1930).

[3] Huggins, *J. Phys. Chem.*, **43**, 1095 (1939).

[4] Garner, van Bibber and King, *J. Chem. Soc.*, 1533 (1931).

[5] Garner, Madden and Rushbrooke, *ibid.*, 2491 (1926).

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The Conversion of Chlorophyll to Pheophytin

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In a previous paper[1] we presented evidence showing the rate of conversion of chlorophyll to pheophytin in 90% acetone was of first order with respect to acid concentration (normality) and possibly of second order with respect to chlorophyll. It was necessary to consider the two chlorophylls as a single component because we did not have the individual components separated. Evidence favored the assumption that the reaction was chiefly a conversion of chlorophyll a to pheophytin a, because the reaction was rarely carried to more than 80% completion. We have now separated sufficient quantities of chlorophylls a and b[2] to repeat previous experiments. Measurements were made at 5350 Å. for chlorophyll a, at 5280 Å. for chlorophyll b, where the respective pheophytin maxima occur.

Results are condensed in Table I. The first and second order rate constants, k_1 and k_2, have been calculated, and each value represents the average of 8–13 determinations over periods of time varying from two minutes to seven hours. The temperature was 28 ± 0.5°. The column Δ indicates the mean deviation of the arithmetic mean of the individual determinations. The values of k/N, whether k_1 or k_2 is taken, clearly show the reaction is of first order with respect to acid concentration, confirming our earlier work.

Table I

Rate Constants for Chlorophyll, in 90% Acetone, with Oxalic Acid

Normality	k_1	Δ	k_2	Δ
		Chlorophyll a		
0.002	0.211	0.046	0.0069	0.0010
.004	.539	.072	.0189	.0099
.007	.907	.088	.0332	.0114
.01	1.39	.170	.0562	.0301
		Chlorophyll b		
0.01	0.148	0.021	0.0040	0.0007
.02	.328	.126	.0088	.0022
.05	.804	.180	.0271	.0049
.10	1.69	.216	.0580	.0148

We were previously at some loss to decide the order with respect to chlorophyll, because in most cases there was an apparent falling off in the calculated constants with time. The k_2 constants for oxalic acid were reasonably constant which led us to suggest a second order for chlorophyll. We knew only that pheophytin b contributed to the absorption at 5350 Å., but we could not then evaluate the extent of its absorption. Because the a and b mixture used was not highly purified, extensive recalculations are not deemed profit-

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[1] Mackinney and Joslyn, This Journal, **60**, 1132 (1938).

[2] Details will be published shortly.

able. Assuming, however, that with 0.002 N oxalic acid, for periods up to five hours, there is no conversion of chlorophyll b, we have recalculated some values on the basis of a 25% inert ingredient, *i. e.*, the chlorophyll b. Under these conditions, the oxalic results fall in line with the others, and we are given little preference between k_1 and k_2 for chlorophyll.

A limitation must be remembered, that with the visual B and L spectrophotometer, we cannot vary our chlorophyll concentrations within a wider range than 3 to 5 times without loss of accuracy. Initial concentrations of chlorophyll in the present experiments were 0.5×10^{-4} M, and the acid varied from 0.01 to 0.002 N for chlorophyll a and from 0.10 to 0.01 N for chlorophyll b.

The present values show no falling off with time, indicating there may be an error inherent in our earlier calculations as there could be no accurate compensation for the effect of chlorophyll b. The k_1/N values are in both cases more constant than those for k_2/N, and in two of the acid levels for chlorophyll b, and in three for a, the deviations are smaller for k_1 than for k_2. Furthermore, there is very little trend in the k_1 values, while in some cases there is a definite upward trend for k_2. We are therefore inclined to believe that the reaction is of first order with respect to both chlorophyll components.

An explanation is required for the fact that with 0.01 N oxalic acid, k_1/N for chlorophyll a has a value of 139, for chlorophyll b, 14.8. If the reactions are correctly interpreted on the basis of first order in both cases, the question arises as to the cause of this difference. We hope to throw further light on this in studies on the removal of magnesium from allomerized components, phytol-free derivatives, and the heats of activation.

Conclusions.—For the pure a and b chlorophyll components, it is confirmed that the reaction involving loss of magnesium is of first order with respect to acid. It is probably of the same order with respect to chlorophyll. The two hydrogens replacing the magnesium must therefore enter at different rates, and in all probability the entrance of the first hydrogen is the rate-governing step. This would materially weaken the remaining magnesium–nitrogen bond, in which respect it would then no longer be equivalent to the initial condition, presumably highly covalent in character.

The chlorophyll a reacts from seven to nine times more rapidly than chlorophyll b.

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The Synthesis of Amino Acids from Benzoylaminomalonic Ester

BY E. P. PAINTER

The use of benzoylaminodiethyl malonate in the synthesis of amino acids as recently reported by Redemann and Dunn[1] has been found to be superior in many respects to the malonic ester and phthalimido malonic ester methods.[2]

The ester alkylates in absolute alcohol with all alkyl halides tried. The ester or derivatives is readily hydrolyzed with constant boiling hydrochloric or hydrobromic acid. Glycine can be isolated in 85% yields by hydrolyzing the free ester with concentrated hydrobromic acid. To the list of amino acids prepared in good yields by Redemann and Dunn by the use of this reagent may be added norleucine, α-amino-γ-phenoxy-n-butyric acid and the lactone of α-amino-γ-hydroxy-n-butyric acid. These have been isolated after hydrolysis of the ester alkylated with n-butyl bromide, β-bromoethyl phenyl ether and ethylene bromohydrin.

In an attempt to prepare β- and γ-halogen amino acids benzoylaminomalonic ester has been alkylated with methylene dibromide, ethylene bromide and ethylene chloride. The products formed contain some halogen but always less than the theoretical amount and the desired amino acids have not been isolated after hydrolysis.

The aminomalonic ester was prepared by the method of Cerchez,[3] excepting the reduction was carried out in alkaline solution with aluminum amalgam made from aluminum turnings and the amino ester benzoylated in a suspension of sodium carbonate in ether saturated with water. By carrying the reaction straight through to the benzoyl compound without isolating the intermediary products, 40–45% over-all yields may be expected. Redemann and Dunn were able to obtain slightly better yields of benzoylaminomalonic ester, but their procedure is more expensive and not as convenient for many laboratories.

The use of anhydrous reagents in alkylations should be emphasized.

[1] Redemann and Dunn, *J. Biol. Chem.*, **130**, 341–348 (1939).

[2] Painter, Ph.D. Thesis, U. of Minnesota, 1939.

[3] Cerchez, *Bull. soc. chim.*, [4] **47**, 1281 (1930).